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Assessment of Perchlorate Releases in Launch Operations II

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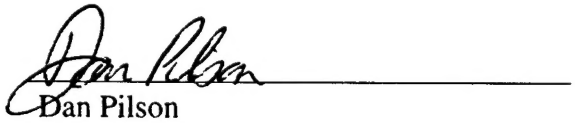

Dan Pilson
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14. ABSTRACT

Laboratory studies were conducted to determine the rates at which perchlorate is released from perchorate-containing solid propellants and the influence of temperature and salinity on the rates. Perchlorate release rates from carboxyl-terminated polybutadiene (CTPB), hydroxyl-terminated polybutadiene (HTPB), polybutadiene-acrylic acid- acrylo-nitrile terpolymer (PBAN), and polyurethane (PU) solid propellants were determined and are reported as diffusion coefficients. The diffusion coefficients for all propellant types and conditions tested were in the range of 3.6×10^{-12} to 1.1×10^{-13} $m^2 s^{-1}$. Modeling studies of solid-propellant debris impacts for Delta IV and Atlas V cases were also conducted using an improved methodology based on the ACTA debris model.

15. SUBJECT TERMS
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Specimens of solid rocket propellant were provided by the Space and Missile Propulsion Branch, Missile Technology Division, Air Force Research Laboratory. We would like to thank Keith McFall for coordinating the effort; John Clark, the team leader; and Adam Irvine and and Chris Cunningham for preparing, characterizing and coordinating shipping of the various propellant specimens required for this project.

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1. Introduction

This report documents progress in the assessment of potential perchlorate releases from launch operations, from a study initiated by the Air Force (AF) Space and Missile Systems Center (SMC) and The Aerospace Corporation. The study was initiated in FY2001 and continued in FY2002. A previous Aerospace technical report[1] included a description of the general regulatory framework regarding perchlorate releases. That report also discussed an interdisciplinary approach to quantifying potential impacts from perchlorate that could be released from launch failures. Two parts of the SMC study, conducted by The Aerospace Corporation are the focus of Sections 2 and 3 of this report:

(1) Determining the rates at which perchlorate is released from perchlorate-containing solid propellants commonly used in U.S. space and sub-orbital launch vehicles, and the influence of temperature and salinity on the rates.

(2) Quantifying the expected amount of solid-propellant debris impacting a launch-site region for a given launch vehicle and a particular flight azimuth.

Regulatory positions and requirements for reporting and monitoring with respect to potential perchlorate releases from launches continue to develop. At least two data requirements from regulatory agencies were filled for AF launches in 2002:

(1) SMC –TR-02-01, Aerospace TR-2001(1306)-3, "Assessment of Perchlorate Releases in Launch Operations,"[1] was submitted to the National Oceanic and Atmospheric Administration, National Marine Fisheries Service with respect to an Essential Fish Habitat consultation for Evolved Expendable Launch Vehicle launches.

(2) A State of Alaska, Coastal Zone Consistency Determination, added ClO_4^- to the list of substances to be monitored in groundwaters at the Kodiak Launch Complex (KLC) before and after launches. This requirement was met for the AF Quick Reaction Launch Vehicle-2 launch in April 2002.

In addition to the Aerospace work, laboratory studies initiated at the University of Alaska during 2002[2] contributed to the interdisciplinary understanding of potential impacts from $ClO4^-$ on environmental receptors relevant to AF launch sites. Specifically, the biological studies included:

- Effects of perchlorate on primary and secondary aquatic production (i.e., on photosynthesis and uptake of amino acid) in freshwater and marine water samples.
- Decomposition processes of perchlorate in marine and freshwater sediments, freshwater wetland peat, and upland soils.
- Effects on the behavior and growth of the fish species the threespine stickleback.

The current overall project plan for the Assessment of Perchlorate Releases in Launch Operations concurs with the Jan 2002 U.S. Environmental Protection Agency (EPA) revised draft toxicity assessment, "Perchlorate Environmental Contamination: Toxicological Review and Risk Characterization."[3] The EPA document is intended to reflect the state of the science regarding health effects of the chemical perchlorate.

One section of the EPA report, Ecological Risk Assessment and Evidence for Indirect Exposure, is particularly relevant to understanding the potential impacts of perchlorate released from launches into soil and water. A peer review of the EPA report held in Sacramento, CA, 5–6 March 2002 found that the ecological impacts section was based primarily on unpublished studies completed since the last EPA review in 1999. Other than a study sponsored by the U.S. Army Corps of Engineers[4] and another unpublished report, the ecological studies completed since 1999 were found to be field screening level reports and therefore not controlled risk assessments. The panel recommendations on the ecological aspects of perchlorate impacts included:

- the need for additional and longer-term studies with amphibians and fish
- the need for analytical methods for lower detection levels in water and tissues
- studies of wild rodent exposure to plants containing perchlorate ion (ClO_4^-)
- mode of action studies on how plants pick up ClO_4^-
- studies of perchlorate transformation in soil and in plants

Results from the SMC studies, which address two of the above issues, are expected to be available from the University of Alaska in the near future. Those results can be used in combination with the release rates and debris quantification methods presented here to better quantify effects from potential releases of perchlorate in launch operations.

2. Chemical Kinetics of Perchlorate Release from Solid Rocket Motor Propellant

2.1 Previous Studies

The purpose of this study is to determine the rate at which perchlorate is released from perchlorate-containing solid propellant and the influence of temperature and salinity on the rate. This study is a follow-up to a 2001 study[1] that reviewed literature and measured the release of perchlorate from a sample of propellant containing hydroxyl-terminated polybutadiene (HTPB) into water at different temperatures and salinities. This study builds on that work with measured release rates from another HTPB propellant of known composition, and rates from three other types of solid propellants. Diffusion is believed to be the limiting process in the perchlorate release mechanism. The perchlorate release rate is presented as a diffusion coefficient that can be used in modeling perchlorate release from propellant. The report begins with a short primer on solid propellants, followed by experimental description, results, diffusion coefficients, and comparison to another study.

2.2 Solid Propellant Overview

Solid propellants[5,6] may be roughly classified by dividing them into general categories based on their composition. Of interest in this study is the composite, a.k.a. composite base, propellants. These are heterogeneous mixtures. The fuel and oxidizer ingredients are present as solid particles that are held together by a solid binder material. A typical example is ammonium perchlorate and aluminum powders held in a synthetic rubber matrix. Composite propellants are usually formulated to fall into the safety rating of non-detonable, DOD Explosive Class 1.3. These propellants may explode if pressurized, confined, or initiated by a detonation, but do not detonate under normal conditions. Most launch systems that use solid boosters use this type of propellant.

The double-base propellants are homogenous mixtures. A typical example is solid nitrocellulose dissolved in nitroglycerin. Both ingredients are explosives. Double-base propellants typically fall into the more hazardous safety rating of detonable DOD Explosive Class 1.1. Ordinary double-base propellants typically do not contain perchlorate. There are propellants that combine characteristics of these two groups. Composite modified double-base propellants are double-base propellants that contain particles of fuel and oxidizer. Typically the oxidizer in composite modified double-base propellants is ammonium perchlorate particles.

Perchlorate-containing composite-base propellants are of interest in this study. Composite-base propellants consist of three main ingredients and several minor ingredients. The main ingredients typically are ammonium perchlorate (AP) oxidizer, aluminum (Al) fuel, and a synthetic rubber binder that holds the propellant together.

Ammonium perchlorate, the oxidizer, is typically present as particles, 20–400 μm, and comprises 50–85% by weight of the total propellant mass. The density of ammonium perchlorate is 1.95g/cm^3.

Aluminum, the fuel, is typically present as spherical particles, 3–100 μm, and comprises 5–21% by weight of the propellant.

The binder holds the ingredients together. There are a number of substances used for binder. The binder is typically 10–20% by weight of the propellant. The density of binder materials ranges from 0.9 to 1.3 g/ cm^3. The binder types are generally not mixed in a single propellant. Some typical binders are hydroxyl-terminated polybutadiene (HTPB), carboxyl-terminated polybutadiene (CTPB), polybutadiene- acrylic acid-acrylonitrile terpolymer (PBAN), and polyurethane (PU).

The binder acronym or name is often the industry jargon for the propellant type. During manufacture, the binder material is added as a liquid that polymerizes to form a rubber-like matrix. It is the binder that has the most effect on the propellant mechanical, aging, and storability characteristics. Binder is suspected to influence the rate of perchlorate release of propellant in water. HTPB is the most commonly used binder.

Several minor constituents make up the balance of material in a composite-base propellant. The curing agent, a.k.a. curing catalyst or crosslinker, causes the propellant mixture to polymerize to a rubber-like solid that adheres to the motor case. The antioxidant/plasticiser, which is less than 1% by weight, is added to improve shelf life of the propellant. Bonding agent, less than 3% by weight, improves adhesion between HTPB binder and the AP particles. This improves the propellant's resistance to stress and strain. The burn rate modifier, a.k.a. burn rate catalyst, is typically an organic or inorganic iron compound that is used to tune the burn rate of the rocket motor to meet specific mission requirements.

HTPB is the most commonly used in modern solid rocket motor systems. PBAN is the propellant used by the STS (shuttle). CTPB and PU are used in Minuteman engines and by the Quick Reaction Launch Vehicles.

Table 2.1 lists some systems that utilize ammonium perchlorate solid propellant. Larger systems generally use solid propellant in strap-on boosters.

Table 2.1. Examples of Systems That Use Ammonium Perchlorate Solid Propellant

Propellant Binder	System
HTPB	Atlas2AS, , Delta IV, Atlas V, Titan IV, Titan II, Orbus1, Conestoga, Pegasus, Taurus
PU	Minuteman I M56A1, QRLV-1
CTPB	Minuteman II SR19, QRLV-2
PBAN	STS (Shuttle), Titan III

2.3 Experimental Study

For this study, small pieces of solid propellant were held immersed in water in individual containers at controlled temperature. Periodically, over the course of several weeks, the containers were opened, and the liquid was analyzed, as described in our previous study,[1] to determine the concentration of perchlorate that had diffused from the propellant. Additionally, observations of the solid propellant's appearance and hardness, before and after the water imersion, are made.

Four types of perchlorate propellant, identified here by their binder type, were used in this study: HTPB, CTPB, PBAN, and PU. Two different batches of HTPB were used. The older batch, which was described in our earlier report,[1] will be referred to herein as HTPB0.

The temperatures used in the study approximate the range of seawater temperatures found from Alaska to Florida, 5, 20, or 29°C. A table of seawater temperatures was provided in our previous report.[1] The experimental water salinity is either deionized (pure) water or a salt-water solution prepared to simulate seawater.

Specimens were prepared by blade cutting and using a blade cork-borer tool. Specimens are cylindrical in shape, with a height of approximately 14 mm and diameter of approximately 14 mm. The weight of each sample was approximately 4 g. The PU is the hardest of the four types of propellant in this study. It was difficult to blade-cut and jammed inside the borer tool. Fewer specimens of PU were used than the other propellant types because of these handling problems. Specimens were immersed in 500 ml, except HTPB0, which was in 250 ml, of deionized water or salt water. The salt water, as in the previous study,[1] was simulated seawater. Actual seawater was not used because it contains biological elements with maintenance requirements beyond the scope of this study. Samples were not actively mixed while being held between analyses, but experienced some mixing effects as a result of vibrations from the temperature-control chambers. Samples were mixed immediately before the withdrawal of an aliquot for analysis. This study did not attempt to measure or control biological conditions. The HTPB specimen at 29°C in salt water is not reported due to a handling error.

Hardness of the specimens was measured with a durometer, which gives an empirical measure of a material's relative resistance to localized plastic deformation. Durometer hardness is commonly used for reporting the hardness of rubber-like materials. The durometer is a handheld, non-electrical device. The hardness value is determined by the penetration of the durometer indenter foot into the sample. There are different scales to cover ranges of hardness. Each scale provides an empirical hardness value that is not correlated to other properties. The correlation between the different durometer scales is weak and so conversion between scales is not made. Durometer readings are unitless, with each scale going from 0 to 100. Readings below 10 and above 90 are generally considered unreliable. Samples were measured prior to immersion on three hardness scales, Type D, Type A, and Type 00. Type D is typically used to measure plastics and hard rubbers, Type A to measure soft rubbers, and Type 00 to measure sponge rubbers.

Measurements were performed with hand-held Pacific Transducer Corporation ASTM 2240 durometers models 409, 306L, and 411 (2.5). Specimens used in this study were smaller than specified by the ASTM procedure.

The propellant samples were provided by the Air Force Research Laboratory, Space and Missile Propulsion Branch, Edwards Air Force Base, California. The HTPB0 sample was known to be 69% ammonium perchlorate. Detailed information on the composition of the other propellant batches is listed in Table 2.2. Table 2.3 summarizes the concentrations, by weight percent, of perchlorate in the specimens used in this study.

Table 2.2. Components of Solid Propellants Used in This Study

HTPB - SRMU-RU5

Al 29μ, aluminum	19.00%
AP 20μ, ammonium perchlorate	19.00%
AP 200μ, ammonium perchlorate	50.00%
DDI, dimeryl diisocyanate	0.25%
IPDI, isophorone diisocyanate	0.52%
R-45M, hydroxyl-terminated polybutadiene	9.03%
AO 2246, 2,2'-Methylene-Bis-(4-Methyl-6-Tert-Butylphenol)	0.09%
DOS, dioctyl sebacate	2.00%
DER 332, epoxy	0.06%
TET, tetra ethyl tetramine	0.04%
TPB, triphenyl bismuth	0.01%

CTPB ANB-3066 MM2nd Stage

AP 200μ, ammonium perchlorate	51.10%
AP 17-20μ, ammonium perchlorate	21.90%
CTPB, carboxyl-terminated polybutadiene	8.56%
Polybutene, Polybutene	3.00%
Al 17-20u, aluminum	15.00%
Butylene imine derivative of trimesic acid	0.44%

PBAN S6-S-1.12 Shuttle

PBAN, polybutadiene acrylonitrile acrylic acid	12.15%
Iron Oxide	0.22%
Al 13μ, aluminum	16.00%
Epoxy resin, Epoxy resin	1.85%
AP 200μ, ammonium perchlorate	48.85%
AP 20μ, ammonium perchlorate	20.93%

PU ANB-2464 HG Mod II

PPG, polypropylene glycol	8.65%
TMG*	4.36%
TEA, Trimesol-1-(2-ethyl) aziridene	0.21%
Carbon black	0.20%
AO-2246, 2,2'-Methylene-Bis-(4-Methyl-6-Tert-Butylphenol)	0.12%
IDP, isodecyl pelargonate	0.27%
DC-200, silicon oil	0.01%
DOZ*	1.73%
AP 200μ, ammonium perchlorate	48.16%
AP 20μ, ammonium perchlorate	17.21%
Al 13μ, aluminum	17.00%
FeAA*	0.04%
TDI, toluene-2,4-diisocyanate	2.05%

*No additional identification available

Table 2.3. Weight Percent of Perchlorate in Propellant Specimens Used in This Study

Propellant Type	Ammonium Perchlorate NH_4ClO_4	Perchlorate ClO_4
CTPB	73.0%	61.8%
HTPB	69.0%	58.4%
PBAN	69.8%	59.1%
PU	65.4%	55.3%

Figure 2.1 shows a photograph of typical specimens prior to immersion. The colors of the HTPB and CTPB are light gray. The PBAN is light gray with a slight reddish color. The PU is dark gray. The appearance of the HTPB and CTPB showed no irregularities. HTPB0 showed no irregularities. The PBAN shows a few small indentations. The PU has numerous holes and indentations, as occur when bubbles form during manufacture.

2.3.1 Perchlorate Release from Propellant

The laboratory measurements of perchlorate concentrations in the water were used to calculate the amount of perchlorate released by the propellant specimen as a fraction of the original mass of perchlorate in the specimen. Measurements for each specimen were repeated over several weeks to provide sufficient data to establish a perchlorate release rate for each specimen at the given temperature and salinity contitions. This data is shown graphically for each propellant in Figures 2.2 through 2.6. On these graphs, the x-axis is plotted as the square root of the time. The data is plotted against the square root of time because this gives a linear fit to diffusion-limited phenomena. The y-axis is the calculated fraction of perchlorate that has left the specimen. A y-axis value of unity would indicate that all perchlorate has left the specimen (although the specimen would still contain perchlorate at a concentration equal to that in the water).

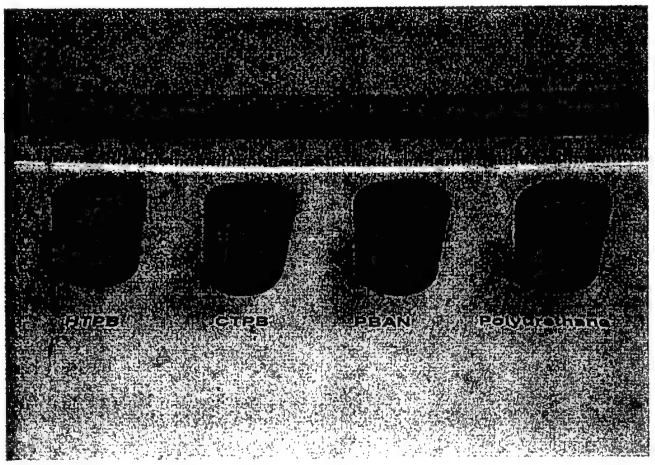

Figure 2.1. Solid propellant specimens prior to immersion in water Left to right, HTPB, CTPB, PBAN, PU.

The results for all propellant types show a correlation of increased rate with increased temperature. For a given specimen type and temperature, the rate of perchlorate release is higher in deionized (pure) water than in salt water. The relative rates of the HTPB, CTPB, PBAN, and PU on the graphs may be directly compared to each other since the sample size, conditions, and water volume were the same. The fastest rate was PU, followed by HTPB, PBAN, and CTPB. The HTPB0 graphs show the same temperature and salinity trends but cannot be directly compared to the other graphs since the water volume, hence the rate of concentration change, is not the same. Data from all of these specimens can be used to calculate a diffusion coefficient for that propellant type, temperature, and salinity condtions. The diffusion coefficient can be used to compare propellants and in modeling perchlorate release.

The results from PU in deionized water at 29°C provide a measure of the experimental error in the method. For this sample, the measurements of perchlorate fraction loss "level off" after 2000 $s^{1/2}$ (approximately 7 weeks). This indicates there is no longer a net extraction of perchlorate from the sample. Nearly all the perchlorate has been extracted from the specimen and the concentration of perchlorate remaining in the propellant is equal to the perchlorate concentration in the surrounding water. This "level off" in the perchlorate fraction loss measurements should, therefore, occur slightly below unity. For this sample, it occurs at 5–10% above unity. This 5–10% difference can be regarded as the experimental error, indicating good accuracy for the method.

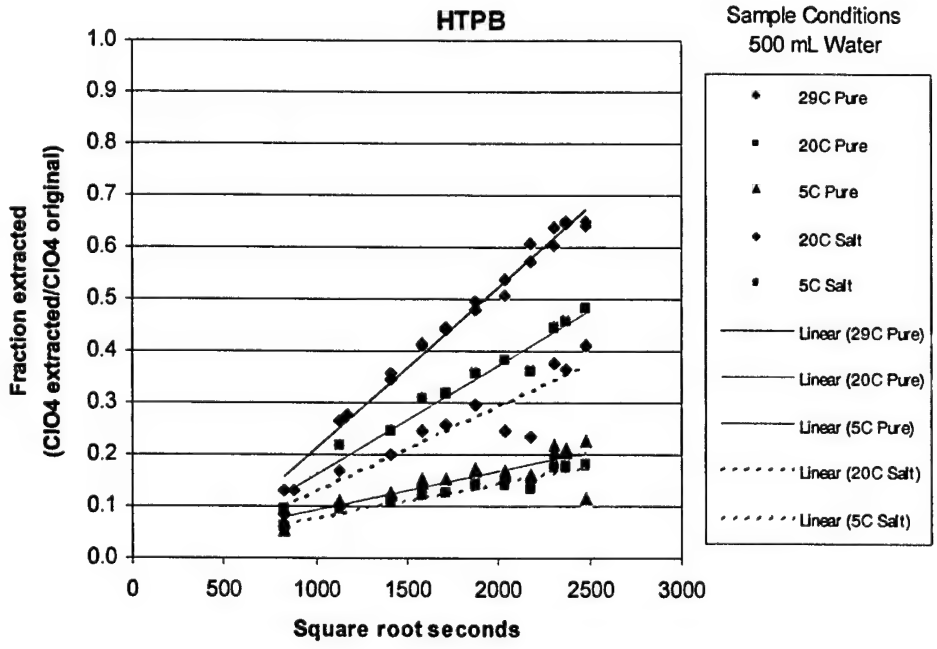

Figure 2.2. Plot of HTPB results. Linear-least-square fit is overlaid on the mass fraction (mass of perchlorate extracted divided by the mass of perchlorate originally in the specimen) vs. immersion time in 500 ml of deionized (pure) or salt water. Data from specimens run under the same conditions are combined in this plot.

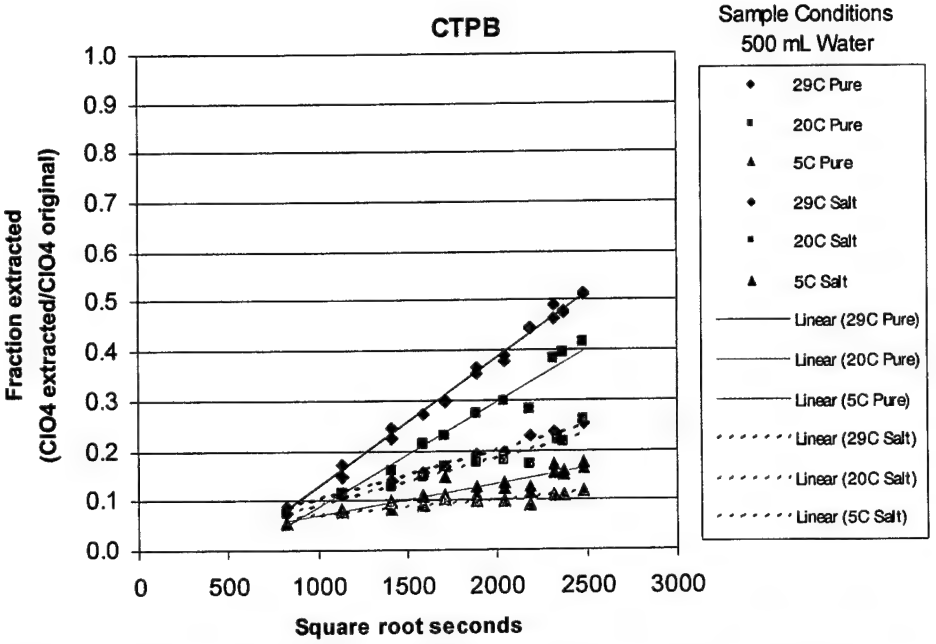

Figure 2.3. Plot of CTPB results. Linear-least-square fit is overlaid on the mass fraction (mass of perchlorate extracted divided by the mass of perchlorate originally in the specimen) vs. immersion time in 500 ml of deionized (pure) or salt water. Data from specimens run under the same conditions are combined in this plot.

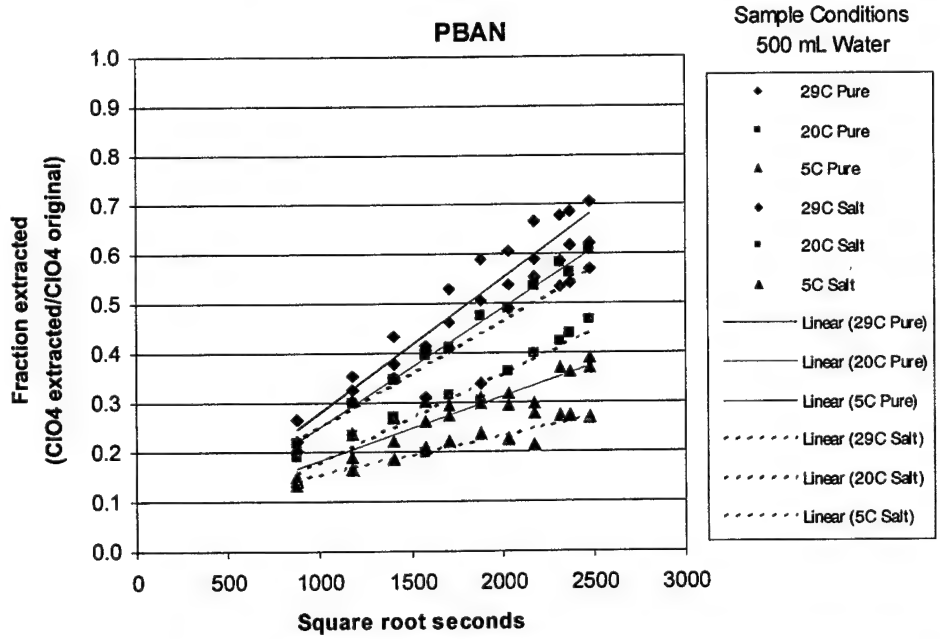

Figure 2.4. Plot of PBAN results. Linear-least-square fit is overlaid on the mass fraction (mass of perchlorate extracted divided by the mass of perchlorate originally in the specimen) vs. immersion time in 500 ml of deionized (pure) or salt water. Data from specimens run under the same conditions are combined in this plot.

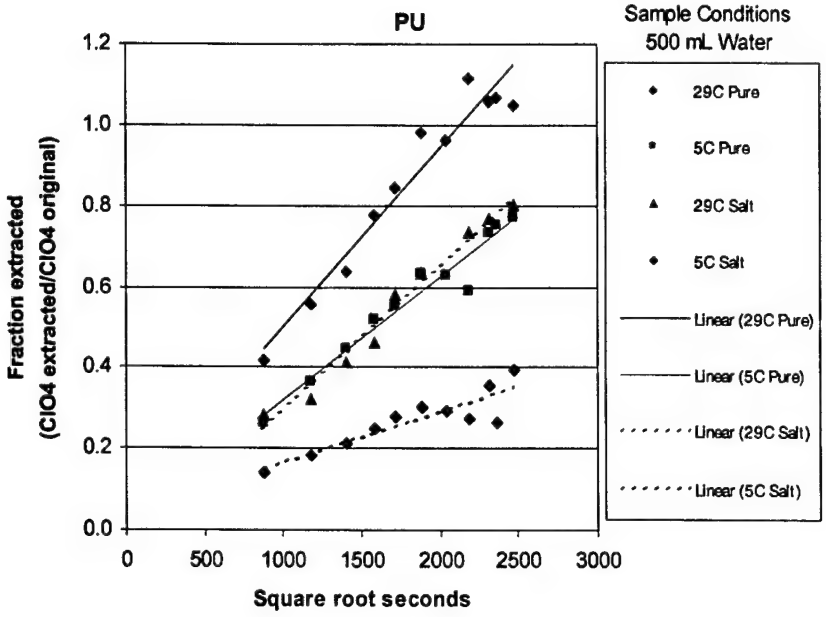

Figure 2.5. Plot of PU results. Linear-least-square fit is overlaid on the mass fraction (mass of perchlorate extracted divided by the mass of perchlorate originally in the specimen) vs. immersion time in 500 ml of deionized (pure) or salt water. Note that the 29°C pure water specimen levels of after 2000 $s^{1/2}$ at a mass fraction of slightly more than 1.0.

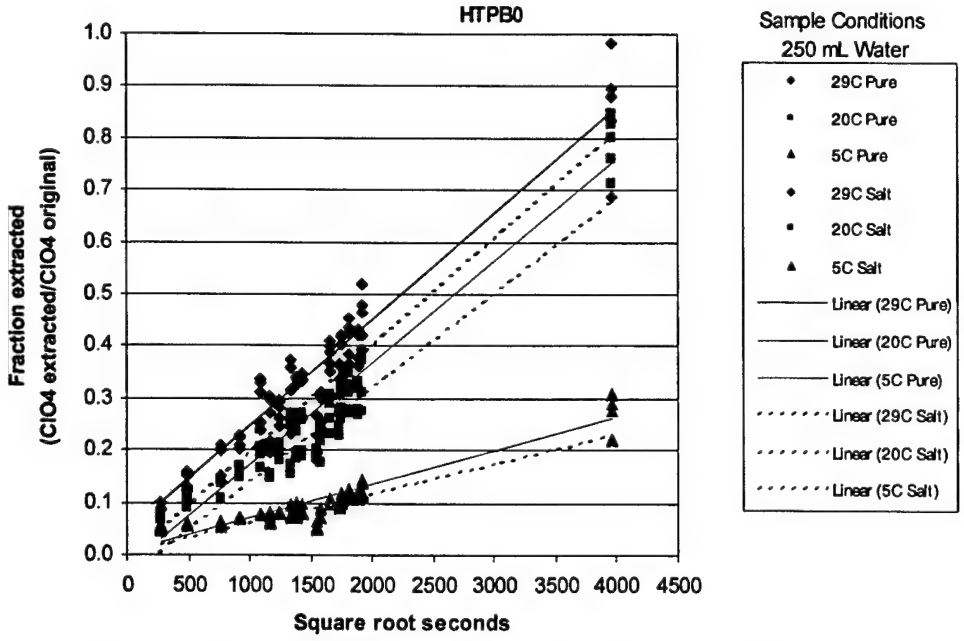

Figure 2.6. Plot of HTPB0 results. Linear-least-square fit is overlaid on the mass fraction (mass of perchlorate extracted divided by the mass of perchlorate originally in the specimen) vs. immersion time in 250 mL of deionized (pure) or salt water. Data from specimens run under the same conditions are combined in this plot.

2.3.2 Effect of Water on Propellant

Following the immersion period, the specimens were inspected for physical changes. The specimens were softer and had increased in volume by various amounts. Hardness of the specimens was measured, and it was determined that hardness of the specimens had lessened from that comparable to hard rubber to that of a soft foam rubber. The color of HTPB and CTPB specimens, dry or wet, are light grays. The slight reddish color of PBAN is more apparent when wet. The PU appears dark gray when dry and black when wet.

Figure 2.7 shows the four types of propellants following immersion under the same conditions. The differing magnitude of volume increase for different propellants is readily apparent. Figure 2.7 can be compared to the unexposed specimens in Figure 2.1. Figure 2.8 is a photograph showing HTPB0 specimens before immersion and after immersion at various temperatures. It can be seen that higher

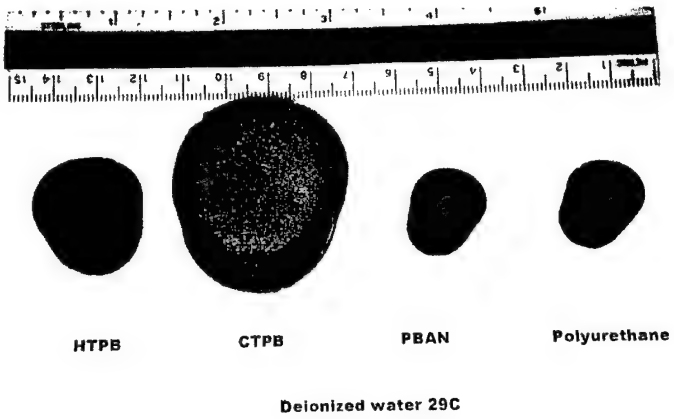

Figure 2.7. Wet solid propellant specimens after 3-month immersion at 29°C in deionized water. Left to right: HTPB, CTPB, PBAN, PU.

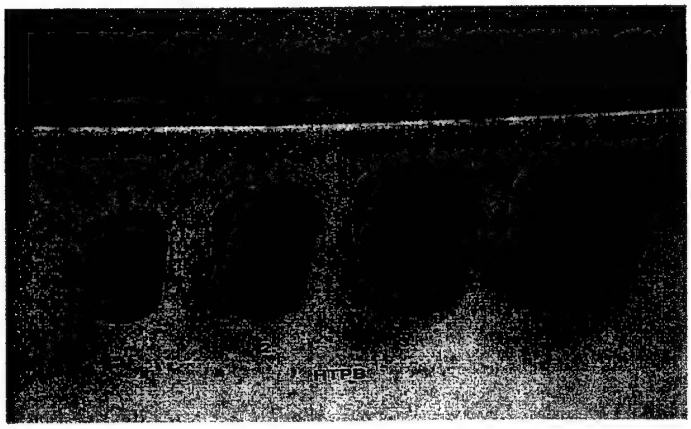

Figure 2.8. HTPB0 propellant specimens immersed for 1 year in deionized water. (1) Not immersed, (2) Immersed at 5°C, (3) Immersed at 20°C, (4.) Immersed at 29°C. The dark areas on the 20°C sample are thought to be evidence of biological activity that clung to the specimen as it was removed from the water.

temperatures correlate with greater volume increase. Figure 2.9 is a photograph of specimens cut to reveal their interior. The specimen on the left shows that the softening and volume increase occur at the surface, while the interior of the specimen may remain hard.

White or dark-colored material was observed in some specimen containers and is thought to be evidence of biological activity. The material did not appear to be attached to the specimens. Some specimens showed no such visible material. Figure 2.10 is a photograph of the material in a specimen container with the immersed propellant specimen.

Figure 2.9. Interior of HTPB0 propellant specimens immersed for 1 year in deionized water. Specimens were sliced to reveal interior. Left to right: Immersed at 5°C, Immersed at 20°C, Immersed at 29°C. The 5°C specimen is sponge-like on the edges and remained hard inside. The hard area is 11.9 mm diameter (the original specimen diameter was 14 mm). The 20°C and 29°C specimens are sponge-like throughout.

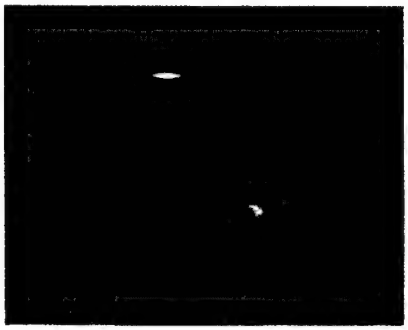

Figure 2.10. An immersed HTPB0 specimen after 1 year. Dark areas are material that appeared in the container, presumed to be evidence of biological activity. Some specimens showed no visible material. The two white areas are reflections. This study did not attempt to measure or control biological conditions

Samples that have been immersed in water increase in size. This is thought to be the effect of water entering and expanding the specimen. The largest diameter increase observed was 210%, this corresponds to a volume increase of over 900%. This was observed for CTPB specimens immersed in deionized water at 29°C. Expansion of specimens in salt water was significantly less than in deionized water at the same temperature. Table 2.4 shows the expansion (final diameter divided by the original diameter) for the size increase based on the increased diameter of the sample after immersion for 1 year. These measurements are not precise; they were made by simply reading a ruler held near the specimen, and are intended to show the general trends.

The measurements (Tables 2.5 and 2.6) show that hardness loss (softening) is greatest at higher temperature and low salinity. This trend correlates with the trend of our measured rates of perchlorate loss from the specimen. This suggests that it may be possible to develop a method for estimating perchlorate concentration in samples.

Table 2.4. Linear Expansion of Propellant Specimens After Immersion in Salt or Deionized Water (Final diameter/Original diameter)

			Water	
Propellant	Duration	Temperature (°C)	Pure	Salt
HTPB0	1 year	29	1.5	1.3
HTPB0	1 year	20	1.5	1.2
HTPB0	1 year	5	1.3	1.0
HTPB	84 days	29	1.4	1.3
HTPB	84 days	20	1.4	1.2
HTPB	84 days	5	1.1	1.0
CTPB	84 days	29	2.1	1.9
CTPB	84 days	20	1.7	1.7
CTPB	84 days	5	1.2	1.1
PBAN	84 days	29	1.0	1.0
PBAN	84 days	20	1.0	1.0
PBAN	84 days	5	1.0	1.0
PU	84 days	29	1.0	1.0
PU	84 days	5	1.1	1.0

Table 2.5. Durometer Hardness of Propellant Specimens Before Immersion. Hardness measurements were taken with durometers of three different scale types, D, A, and 00.

Sample ID	Type D Model 409	Type A Model 306L	Type 00 Model 411
HTPB	18.5	52.5	92.0
CTPB	26.0	85.0	94.5
PBAN	24.5	83.5	92.5
PU	44.5	90.5	95.0

Table 2.6. Durometer 00 Hardness Measurement of Propellant Specimens Immersed in Deionized and Salt Waters

Propellant	Duration	Temperature (°C)	Water	
			Deionized	Salt
HTPB0	1 year	29	32	35
HTPB0	1 year	20	34	39
HTPB0	1 year	5	55	64
HTPB	84 days	29	18	36
HTPB	84 days	20	41	59
HTPB	84 days	5	66	67
CTPB	84 days	29	0	0
CTPB	84 days	20	0	0
CTPB	84 days	5	42	59
PBAN	84 days	29	73	66
PBAN	84 days	20	56	68
PBAN	84 days	5	77	69
PU	84 days	29	58	71
PU	84 days	5	67	78

2.4 Determination of Diffusion Coefficients

Diffusion is the process whereby material is transported as a result of random molecular motion. Although individual molecules move randomly, there is an average movement from areas of high concentration to areas of low concentration. The Einstein-Smoluchowski Eq. (1) gives the root-mean-square (rms) distance traveled by a diffusing molecule and shows the square-root relationship characteristic of the process.

$$(\Delta x)_{rms} = \sqrt{2Dt}\,, \tag{1}$$

where Δx is the distance traveled, D is the diffusion coefficient, and t is time.

Diffusion coefficients[7,8,9] for the release of perchlorate from solid propellant immersed in water were calculated from the lab data analytically using Bessel function series assuming Fickian Diffusion for HTPB, CTPB, PBAN, and PU. Diffusion coefficients for HTPB0 were calculated numerically as a Fourier series. Mathcad and Excel software programs were used in the calculations. Tables 2.7 through 2.11 list the diffusion coefficients for the five batches of propellants tested.

Table 2.7. CTPB Diffusion Coefficients

Temperature	Water	
(°C)	Deionized	Salt
29	1.3E-12	8.6E-13
	1.3E-12	
20	9.9E-13	4.3E-13
5	4.0E-13	1.4E-13
	3.6E-13	

Table 2.8. HTPB Diffusion Coefficients (m^2s^{-1})

Temperature	Water	
°C	Deionized	Salt
29	1.5E-12	
	1.5E-12	
20	1.1E-12	7.7E-13
5	3.9E-13	2.8E-13
	3.7E-13	

Table 2.9. HTPB0 Diffusion Coefficients (m^2s^{-1})

Temperature	Water	
(°C)	Deionized	Salt
29	1.7E-12	1.1E-12
20	8.5E-13	7.5E-13
5	1.4E-13	1.1E-13

Table 2.10. PBAN Diffusion Coefficients (m^2s^{-1})

Temperature	Water	
(°C)	Deionized	Salt
29	1.8E-12	1.2E-12
	1.4E-12	
20	1.3E-12	8.3E-13
5	6.0E-13	4.2E-13
	6.9E-13	

Table 2.11. PU Diffusion Coefficients (m^2s^{-1})

Temperature	Water	
(°C)	Deionized	Salt
29	3.6E-12	1.8E-12
5	1.3E-12	5.4E-12

The diffusion coefficient can be employed to model propellant perchlorate release. The characteristic diffusion time corresponds to the time required for a concentration decrease to 1/e of its original value.[10] For a sphere, this time can be calculated from the following expression:[11]

$$t = \frac{r^2}{\pi^2 D}, \tag{2}$$

where t is the characteristic diffusion time, r is the sphere radius, and D is the diffusion coefficient.

For materials that have a constant diffusion coefficient, this expression can be used to calculate the characteristic diffusion time for spheres of various radii.

This concentration decrease to 1/e of its original value equates to a release of approximately 63% of the perchlorate from the sample. Fitting this amount as a linear function of the square root of the characteristic diffusion time provides a means to calculate the fraction loss of perchlorate at various times.

The Arrhenius expression[12] can be used to extrapolate diffusion coefficients at other temperatures. The relationship of rate constants with temperature is given by

$$k = Ae^{-E_a/RT}, \tag{3}$$

where k is the rate constant, in this case the diffusion coefficient; A is the pre-exponential factor; E_a is the activation energy; T is temperature in Kelvin; and R is the molar gas constant.

In this case, the value obtained for the activation energy probably reflects a composite of Van der Waals barriers, viscosity, and binder lattice temperature effects of a perchlorate ion moving from one position to the next. Activation Energies[12] calculated for each propellant are shown in Table 2.12.

The Arrhenius expression provides a linear relationship between the logarithm of rates and the inverse of their absolute temperature. Figure 2.11 shows an Arrhenius plot for the diffusion coefficients of HTPB in deionized water and in salt water.

Tabel 2.13 lists the terms of a least-squares fit to an Arrhenius plot for each type of propellant tested, in salt and in deionized water. One can use the terms from the line fit to calculate diffusion coefficients at various temperatures.

Table 2.12. Activation Energies [Ea (kcal mol^{-1})]

Water	HTPB0	HTPB	CTPB	PBAN	PU
Deionized	17.6	9.7	8.4	6.3	6.3
Salt	16.6	11.0	12.3	8.7	7.7

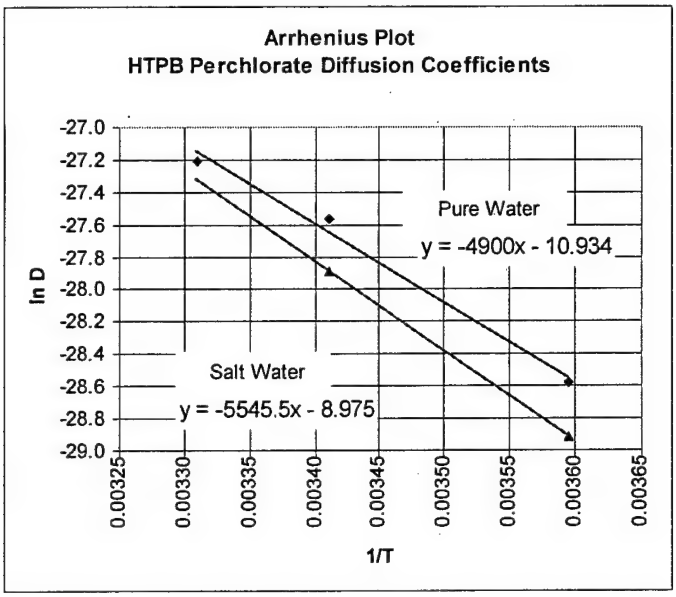

Figure 2.11. Arrhenius plot of HTPB0 diffusion coefficients in deionized and salt water.

Table 2.13. Terms for Arrhenius Fit of Diffusion Coefficients

		ln D=m (1/t) + b	
Propellant	**Water**	**m**	**b**
HTPB0	Deionized	–8.872E+03	2.342
HTPB0	Salt	–8.350E+03	0.279
HTPB	Deionized	–4.900E+03	–10.934
HTPB	Salt	–5.545E+03	–8.975
CTPB	Deionized	–4.208E+03	–13.366
CTPB	Salt	–6.203E+03	–7.264
PBAN	Deionized	–3.169E+03	–16.604
PBAN	Salt	–4.371E+03	–12.883
PU	Deionized	–3.171E+03	–15.860
PU	Salt	–3.851E+03	–14.287

Calculations of characteristic diffusion time based on diffusion coefficients obtained for HTPB and HTPB0 in salt water can be compared to the values obtained by extrapolating data from a study conducted by Merrill[13] of an HTPB propellant in seawater. That experiment studied 1-, 2-, and 4-in. cubes of an HTPB propellant in a 10,500 gallon pool of seawater at an average temperature of 71.5°F. The experiment stopped before the 1/e time was reached, but that time may be estimated by extrapolating the existing data against the square root of time. Good agreement is shown when this data is compared to calculated characteristic diffusion times of 1-, 2- and 4-in.-dia spheres using the diffusion coefficients for HTPB and HTPB0 specimens adjusted for temperature.

Table 2.14. Comparison of Calculations of Characteristic Diffusion Time Using Diffusion Coefficients Obtained for HTPB, HTPB0 in Salt Water to the Values Obtained by Extrapolating Data From Merrill Study of an HTPB Propellant In Seawater

Calculated from Diffusion Coefficients (s)			From other HTPB study (s)	
Sphere, diam (in.)	HTPB salt water	HTPB0 salt water	Cube, edge (in.)	Seawater
1	1.9E+07	2.4E+07	1	2.2E+07
2	7.5E+07	9.6E+07	2	5.7E+07
4	3.0E+08	3.8E+08	4	2.6E+08

2.5 Summary of Experimental Results

The perchlorate diffusion coefficients have been measured for samples of HTPB, CTPB, PBAN, and PU solid rocket motor propellant in deionized water and simulated seawater. The diffusion coefficients for all propellant types and conditions tested fall in the range of 3.6×10^{-12} to 1.1×10^{-13} $m^2 s^{-1}$. The diffusion coefficients for each propellant type are proportional to temperature and inversely proportional to salinity. Arrhenius terms were presented to facilitate calculation of the diffusion coefficient at intermediate temperatures. Characteristic diffusion times calculated for 1-, 2-, and 4-in.-dia spheres of HTPB were compared with another study. The amount of softening and volume enlargement of the solid propellant as a result of water immersion varies greatly between propellant types and shows a correlation with temperature and an inverse correlation with salinity.

3. Launch Failure Analyses

3.1 Comparison with Previous Studies

A previous technical report[1] described the methodology developed at The Aerospace Corporation to quantify the probability of solid-propellant impact over a particular region, assuming early launch failure of DOD launch vehicles. This methodology can be used to predict the mass of solid propellant (and thus perchlorate) that will be released if a failure occurs anywhere along the launch trajectory. In this report, an improved methodology is illustrated for Delta IV and Atlas V cases.

Four improvements were made to the original methodology. First, we changed our methodology for calculating the crossrange and downrange impact probability. Previously, the standard deviation was derived from historical sources (such as Titan). For this study, we used Monte Carlo analyses to determine standard deviations. Second, we used drag impact points instead of vacuum impact points for the distribution. Third, we investigated the solid debris model provided by ACTA Inc.[15] It was determined that this model handled the burning of the propellant in an appropriate manner. Fourth, we now represent weight instead of impact probability in the final presentation of results.

3.2 Methodology for Creating Solid Propellant Impact Probability Distributions

It is desired to estimate the expected amount of solid propellant debris impacting the launch site region for any given launch failure. The methodology described in this section quantifies this expected amount given a particular vehicle and a particular flight azimuth for impact areas that are 15 x 15 arc seconds. Debris models, debris distributions, and trajectory data are used to compute expected weight, the results are presented in the form of a debris map.

The expected weight ($E[W]_i$)of solid propellant that will impact the ith arbitrary area in the time interval (Δt) can be written as:

$$E[W]_i = \Delta t \times P_{Frate} \times nfrag \times \int_{x_i-\frac{\Delta x_i}{2}}^{x_i+\frac{\Delta x_i}{2}} \int_{y_i-\frac{\Delta y_i}{2}}^{y_i+\frac{\Delta y_i}{2}} f(x,y)dydx. \quad (1)$$

A brief description of each of the terms in Eq. (1) is given here; a more detailed description of the values that will be used for specific cases is given in the Case Studies Subsection 3.3. P_{Frate} is the vehicle failure rate with units of 1/s. The terms x_i and y_i are the distances from the nominal impact point to the center of the ith area. The terms Δx and Δy represent the downrange and crossrange dimensions of the ith area. The term *nfrag* is the number of solid propellant fragments that will be created if there is a failure in the given time interval. The term $f(x,y)$ is the probability density function in the downrange (x) and crossrange (y) directions. For this methodology, $f(x,y)$ is assumed to be

a normal bivariate distribution in the crossrange and downrange directions. A Gaussian distribution is chosen because there are many random events leading to a launch vehicle failure. The standard deviations for the distribution are chosen based on Monte Carlo analysis using wind dispersions, imparted velocity dispersions, malfunction turn data, and performance dispersions.

Equation (1) is applied to the midpoint between two discrete impact points (IP) obtained from the trajectory data. The impact points are calculated using a trajectory simulation program, where the vehicle thrust is terminated, and the fragment is simulated to ground impact. Judgement is used to determine the spacing of these discrete points. For the early portion of the boost, a 5-, 10-, or 15-s interval is used. This interval is the dwell time, Δt. If multiple time intervals are being evaluated, the expected weights for impact areas can be summed.

3.3 Case Studies

Three cases have been selected as examples: two Delta IV-M(5,4) missions and an Atlas V (551). As is discussed in Subsection 3.2, the inputs for these case studies are the debris models, the failure probabilities, and the crossrange and downrange standard deviations as a function of the time interval.

The solid-propellant debris models indicate that there exists no significant debris impacting the ground (or ocean) for any catastrophic failure occurring after 40 s for Delta IV and 35 s for Atlas V. This is due to the fact that propellant is assumed to continue burning as it falls to the ground. Failures occurring before these times will result in solid propellant debris impacting the ground. Features of the debris model are discussed in Subsection 3.5. Since the likelihood of failure during the initial boost phase is difficult to assess, the risk of SRM debris impact in the launch area is quantified as a conditional probability. Simply stated: "Assume there is a catastrophic failure of the launch vehicle during the initial 35 or 40 s (depending on the launch vehicle) of flight, then determine the expected weight of solid propellant to impact within each grid cell." Under this condition, P_{Frate} is set to 1/(40s) for Delta IV and 1/(35s) for Atlas V.

The debris fragments can generally be categorized in the following manner: 50% weigh less than 10 lb, 35% weigh between 10 and 100 lb, and 15% weigh more than 100 lb.

The standard deviations for the impact distribution are estimated using a Monte Carlo trajectory simulation technique that computes dispersed impact locations due to winds, imparted velocity, vehicle guidance/performance errors, and vehicle malfunction turns. Impact dispersions are calculated in the following manner. A launch vehicle trajectory-modeling program is used to simulate either a nominal ascent, an off-nominal ascent due to a guidance error, or a malfunction turn to a destruct point. From the destruct point on the trajectory, a velocity is imparted in a random direction, and then the fragment's fall is simulated in the presence of a statistical profile wind to determine the drag impact dispersion location. Figure 3.1 displays the results (i.e., the impact locations) of the Monte Carlo analysis. In this example, over 10,000 failure trajectories were modeled. For each random sample, the destruct time, imparted velocity to the fragment, and fragment ballistic coefficient are selected based on the debris model information.

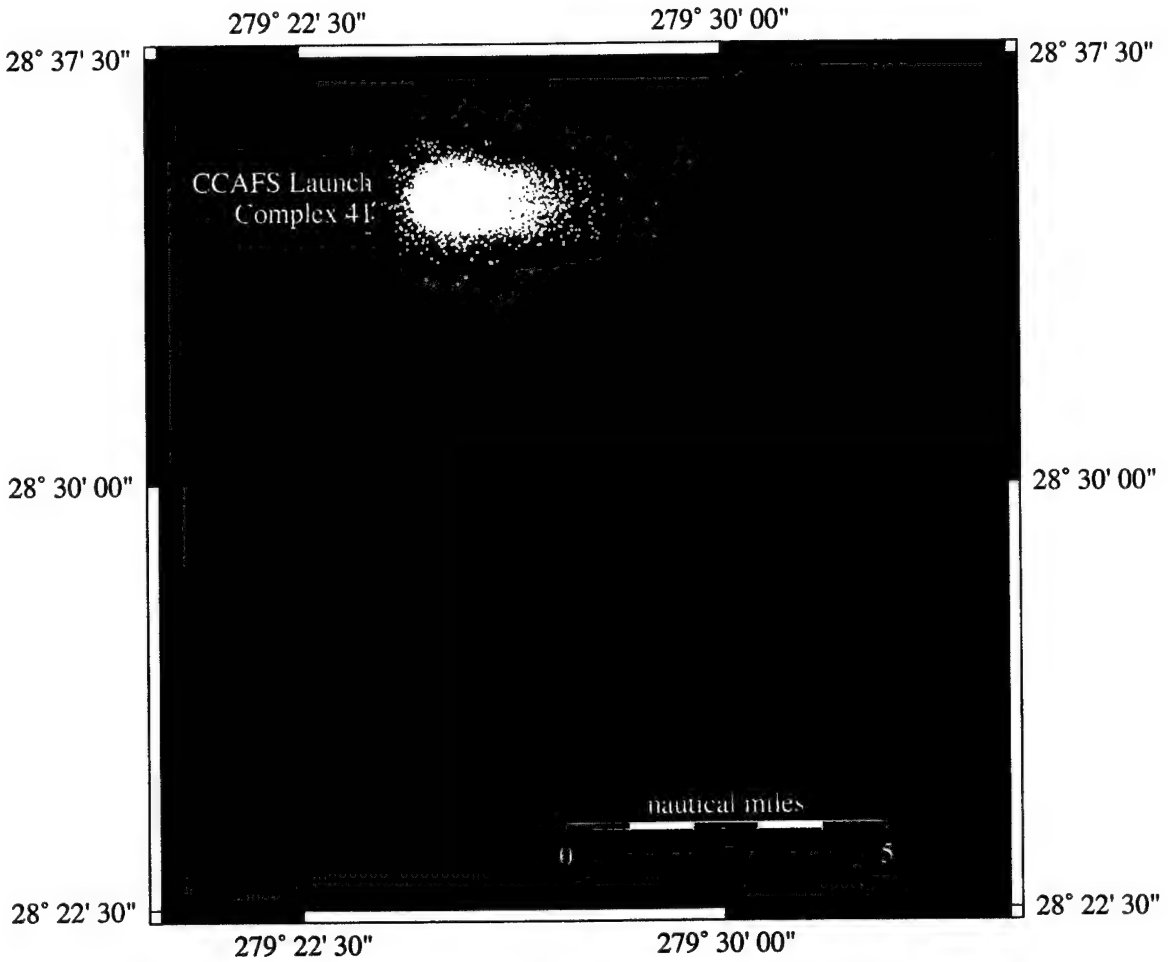

Figure 3.1. Solid propellant fragment impact locations from Monte Carlo analysis; East-coast launch failure of Atlas V 551.

3.3.1 West Coast Delta IV-M(5,4)

The Delta IV-M(5,4) case consists of a Delta IV common core with 4 GEM 60 solid-propellant motors launched from VAFB, Space Launch Complex 6 (SLC-6). There are also variants of the Delta IV that have 2 GEM 60 solid motors; the second number in the parenthesis represents the number of solid motors. The launch azimuth for the chosen mission is 180°.

The debris model for the GEM 60s is shown in Table 3.1 as a function of time. This data is a simplified version of the debris model in Ref. 15, which is a debris model that takes into account the burning of propellant as it falls to the ground. The ballistic coefficient and imparted velocity from the debris model are used within the Monte Carlo trajectories to calculate crossrange and downrange dispersions.

The crossrange and downrange dispersions for debris impact are shown in Table 3.2.

Eq. (1) is used to calculate the expected weight that will impact each 15 x 15 arc-second cell, as shown in Figure 3.2. It can be seen that the highest expected weight occurs very near the launch pad with the weight decreasing outward, generally in the shape of concentric ellipses. In this case, the

Table 3.1. Solid-Propellant Debris Model Over Time for Delta IV-M (4 SRMs)

Debris Class	Number of Fragments	Ballistic Coefficient (lb/ft^2)	Imparted Velocity (ft/s)
0–15 s			
<10 lb	624	106	169
10–100 lb	652	186	126
> 100 lb	332	285	100
15–25 s			
<10 lb	616	90	149
10–100 lb	196	181	119
> 100 lb	72	235-316	119
25–30 s			
<10 lb	584	68	141
10–100 lb	176	137	121
> 100 lb	58	176-221	121
30 – 35 s			
<10 lb	156	119	119
10-100 lb	36	149	119
> 100 lb	8	170-178	119
35 – 40 s			
<10 lb	8	161	120
10-100 lb	0	N/A	N/A
> 100 lb	0	N/A	N/A

Table 3.2. One-Sigma SRM Fragment Impact Dispersions Over Time

Debris Class	$\sigma_{crossrange}$ (nmi)	$\sigma_{downrange}$ (nmi)
0–15 s	0.25	0.25
15–25 s	0.35	0.4
25–30 s	0.45	0.55
30–35 s	0.55	0.65
35–40 s	0.65	0.75

highest expected weight for a single cell is 7,000 lb. It must be remembered that it was assumed that a failure occurs in the first 40 s after liftoff. The expected propellant weight vanishes downrange due to the assumption that all the fuel fragments will burn to depletion for failures after launch +40 s. Non-propellant debris fragments have debris patterns that extend beyond this time interval.

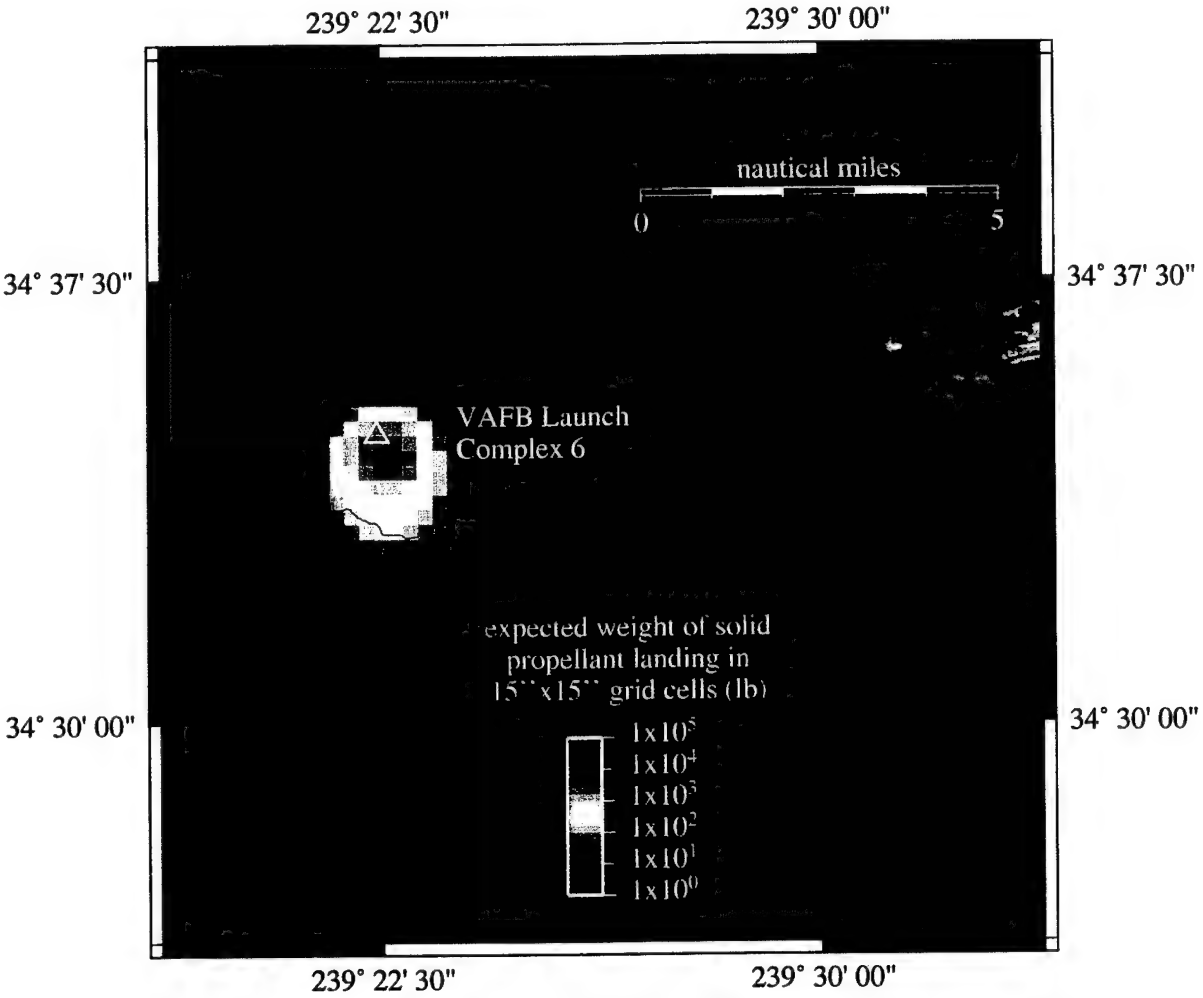

Figure 3.2. West-coast launch failure of Delta IV-M(5,4); expected propellant weight for 15 x 15 arc-s cells.

3.3.2 East coast Delta IV-M(5,4)

The launch azimuth is 95°, typical for a geosynchronous transfer orbit mission. Tables 3.1 and 3.2 also apply. Figure 3.3 displays the expected propellant weight for this mission. Once again the highest expected weight for a single cell is around 7,000 lb.

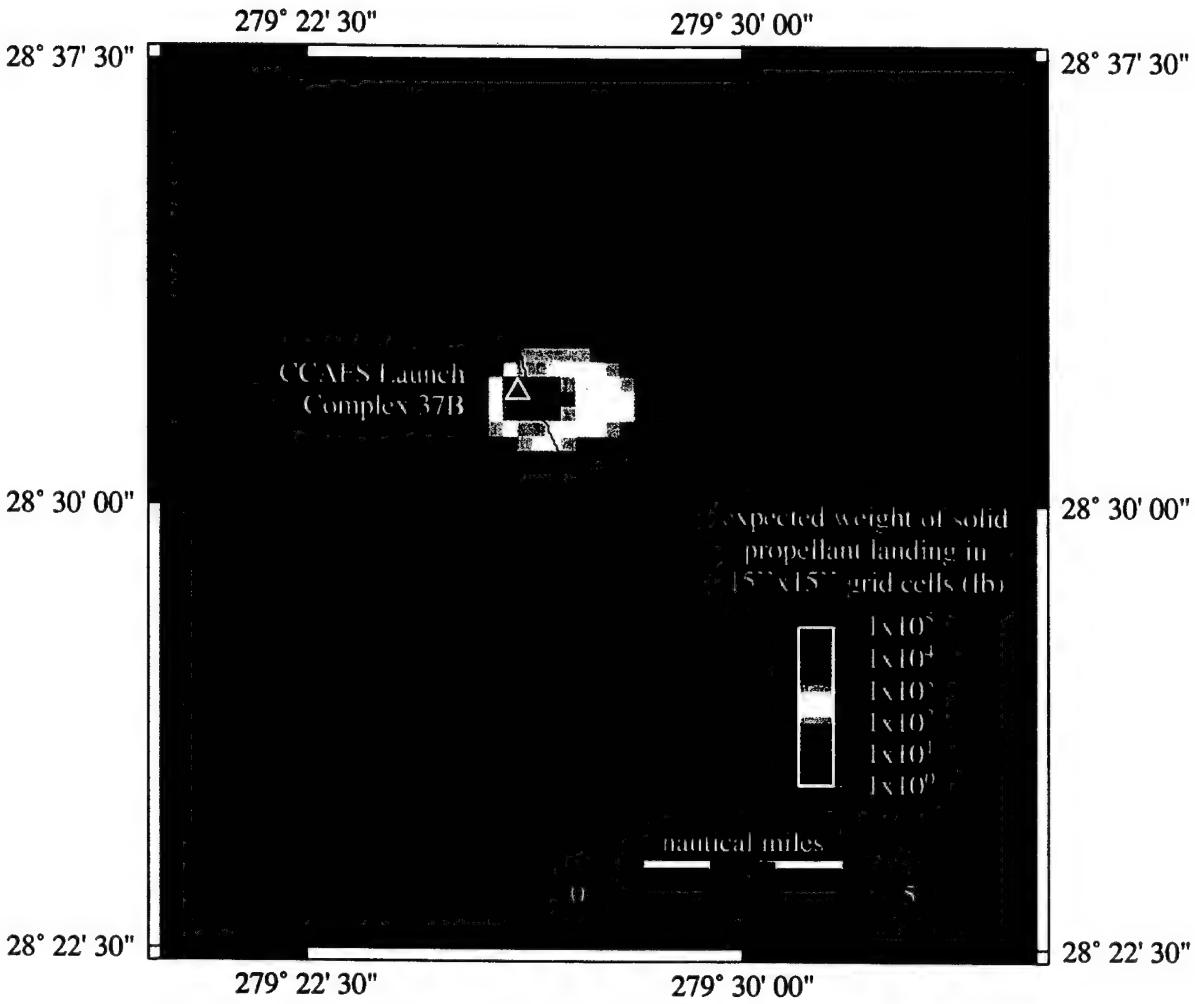

Figure 3.3. East-coast launch failure of Delta IV-M(5,4); expected propellant weight for 15 x 15 arc-s cells.

3.3.3 East coast Atlas V 551

The launch azimuth is 95°, typical for a geosynchronous transfer orbit mission. A vehicle failure in the initial 35 seconds was assumed. The debris and dispersions are given in Tables 3.3 and 3.4, respectively. Figure 3.4 displays the expected propellant weight for this mission. The highest expected weight for a single cell is around 14,000 lb.

Table 3.3. Solid Propellant Debris Model Over Time for Atlas V 551 (5 SRMs)

debris class	number of fragments	ballistic coefficient (lb/ft^2)	Imparted velocity (ft/s)
0–10 s			
<10 lb	925	127	192
10–100 lb	885	230	141
> 100 lb	435	355	107
10–20 s			
<10 lb	920	61	257
10–100 lb	845	110	189
> 100 lb	370	219	171
20–30 s			
<10 lb	810	86	187
10–100 lb	245	166	184
> 100 lb	90	205	184
30–35 s			
<10 lb	55	146	195
10–100 lb	15	160	195
> 100 lb	0	N/A	N/A

Table 3.4. One-sigma SRM Fragment Impact Dispersions over Time

debris class	$\sigma_{crossrange}$ (nmi)	$\sigma_{downrange}$ (nmi)
0–10 s	0.25	0.25
10–20 s	0.35	0.4
20–30 s	0.5	0.55
30–35 s	0.65	0.75

3.4 Using the Results

The data created using this methodology is applicable only to these specific launch vehicles at these same flight azimuths. However, the results are representative of a typical impact probability distribution for any launch vehicle that has SRMs. The major determining factors are the vehicle failure rate and the number and size of solid propellant fragments as a function of destruct time. If need be, these results can be scaled to similar vehicles with the same solids. An example would be to take the Delta IV-M(5,4) results and divide *nfrag* in Eq. (1) by 2 to represent the Delta IV-M(5,2), with the assumptions that the overall fragment number is one-half, and that the same vehicle failure rate and a similar trajectory apply. The azimuths chosen are typical flight azimuths for the vehicle. Also, as the flight azimuth is rotated, the probability distribution would essentially rotate along with it according to the ground trace.

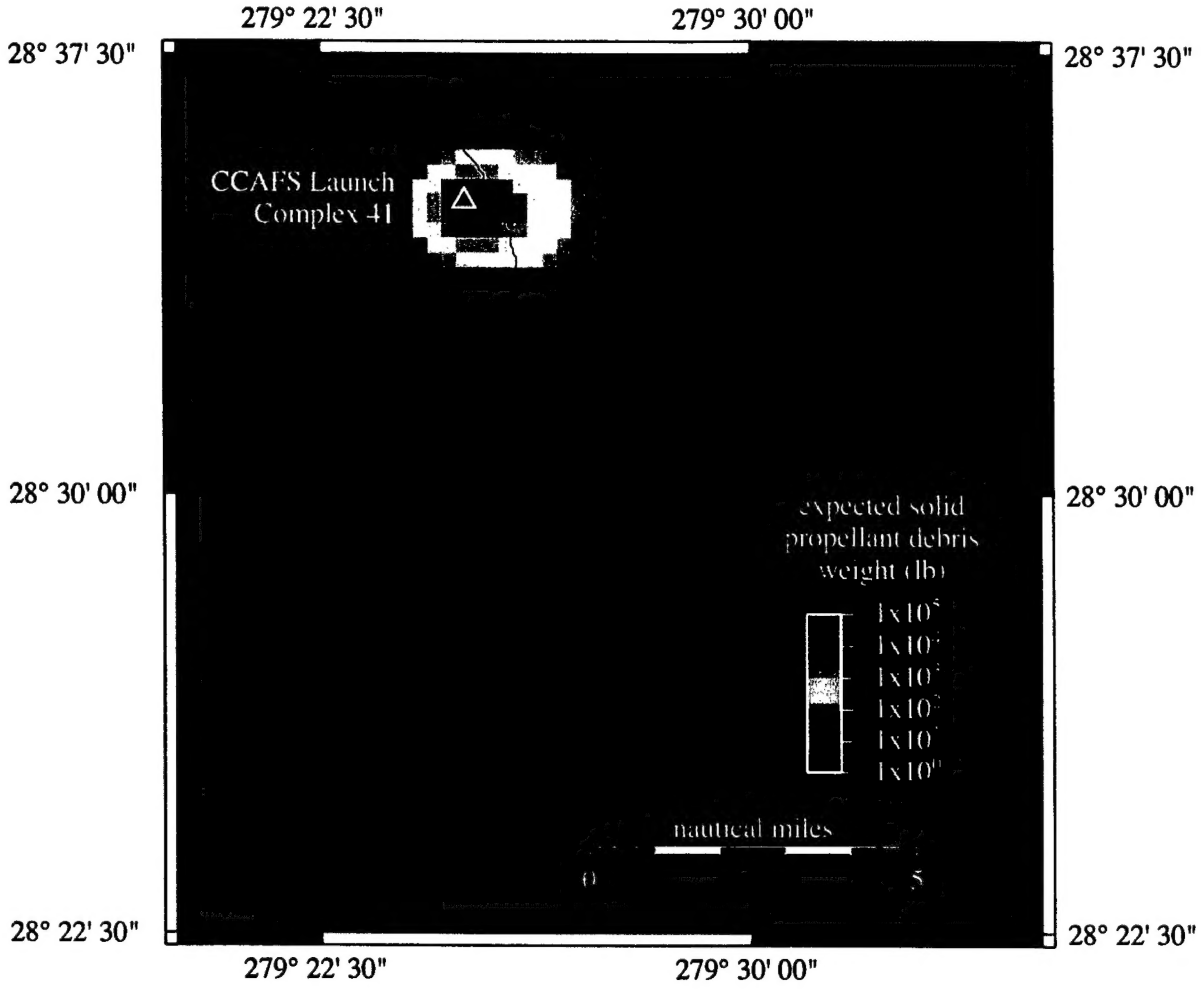

Figure 3.4. East-coast launch failure of Atlas V 551; expected propellant weight for 15 x 15 arc-s cells.

3.5 Solid Propellant Debris Model Discussion

The solid propellant debris models in Tables 3.2 and 3.4 are taken from models created by ACTA, Inc. Because the results of the present study depend on the assumptions for this debris model, a discussion of the model is given. Questions that arise are: Will debris burn after the failure? Is an appropriate burn rate being used? Are the fragment sizes appropriate?

The ACTA debris model assumes that there is a failure due to a commanded destruct or range safety destruct using the on-board flight termination system. This is a valid assumption given that the majority of failures are of this type.

The ACTA debris model assumes that all solid propellant debris is ignited upon failure. However, in most applicable launch vehicle failures, burning and non-burning propellant is observed on the ground immediately following the failure. For example, the Delta 241 failure investigation report[14] stated that 2500 pieces of solid propellant were found on the ground following failure. Many were

burning, but some were not. Currently, no work has been done to calculate the percentage of propellant that is burning, so assuming all propellant is burning might be too liberal of an assumption.

The ACTA debris model uses burn rates of about 0.06 in./s at 1 atm; this is in good agreement with experimental data available.

ACTA assumes that the largest fragment is 8% of the total propellant mass and that the smallest size is a 2-in. cube. The accuracy of this assumption is difficult to assess.

3.6 Summary

By combining a solid propellant debris model with the methodology described in Subsection 3.2, a launch area map showing the expected weight of SRM debris can be produced. The results assume a failure early in the boost phase for a specified launch vehicle and pad. This propellant debris mapping could then be used as input to a perchlorate release study for that region.

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